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(71) Applicant *(for all designated States except US)*: ISOVER SAINT-GOBAIN [FR/FR]; Les Miroirs, 18, avenue d'Alsace, F-92400 Courbevoie (FR).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: ROUYER, Elisabeth [FR/FR]; 32bis, rue de l'Alma, F-92600 Asnières (FR). DE MERINGO, Alain [FR/FR]; 294, rue Saint-Jacques, F-75005 Paris (FR). HOLSTEIN, Wolfgang [DE/DE]; Herderstrasse 2, D-67744 Homberg (DE). MAUGENDRE, Stéphane [FR/FR]; 21, rue Gaston Watteau, F-60460 Précy-sur-Oise (FR).

(74) Agent: KADOR & PARTNER; Corneliusstrasse 15, D-80469 München (DE).

(54) Title: GLASS-FIBER COMPOSITIONS

(57) Abstract

A biologically degradable mineral-fiber composition characterized by the following constituents in percent by weight: SiO_2 50 to 60; Al_2O_3 less than 2; $CaO + MgO$ 10 to 16; $Na_2O + K_2O$ 14 to 19; B_2O_3 7 to 16; TiO_2 0 to 4; ZrO_2 0 to 5; ZnO 0 to 5; MnO 0 to 4; BaO 0 to 5; TiO_2, ZrO_2, ZnO, MnO, BaO 1 to 6; Fe_2O_3, SrO 0 to 2; F, Li_2O 0 to 2; P_2O_3 0 to 4.

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Glass-fiber compositions

The present invention relates to a glass-fiber composition that is biologically degradable.

The prior art describes some glass-fiber compositions which are said to be biologically degradable.

The biological degradability of glass-fiber compositions is of great importance because various studies point out that some glass fibers with very small diameters in the range of less than 3 microns may be carcinogenic, while biologically degradable glass fibers of such dimensions show no carcinogenicity.

However not only the biological degradability is of crucial importance but also the mechanical and thermal properties of the glass fibers, or the products produced therefrom, the resistance of the glass fibers and the processibility of the glass-fiber composition. For example glass fibers are used to a great extent for insulation purposes. For these applications sufficient moisture-resistance is necessary.

Also, the glass-fiber composition must permit processibility by known methods for producing glass fibers with a small diameter, for example the centrifugal technique, in particular the inner centrifugal technique (this technique is described for example in US-PS 4 203 745).

The invention is based on the problem of providing a novel glass-fiber composition that is characterized by biological degradability, has good stability or resistance to moisture and is easy to process.

The invention is based on the finding that this problem can be solved by a glass-fiber composition that comprises considerable amounts of alkali oxides and boron oxide, and contains titanium oxide, zirconium oxide, zinc oxide, manganese oxide, barium oxide or mixtures of two or more of these oxides.

It has turned out that such a glass-fiber composition fulfills the combination of the necessary properties, namely biological degradability, resistance to moisture and good processibility.

The object of the invention is a glass-fiber composition that is biologically degradable, characterized by the following constituents in percent by weight:

SiO_2	50 to 60
Al_2O_3	less than 2
$CaO + MgO$	10 to 16
$Na_2O + K_2O$	14 to 19
B_2O_3	7 to 16
TiO_2	0 to 4
ZrO_2	0 to 5
ZnO	0 to 5
MnO	0 to 4
BaO	0 to 5
TiO_2, ZrO_2, ZnO, MnO, BaO	1 to 6
Fe_2O_3, SrO	0 to 2
F, Li_2O	0 to 2
P_2O_3	0 to 4.

The inventive glass-fiber compositions are processible by the centrifugal technique. The obtained fibers have good resistance to moisture. Surprisingly enough, the glass-fiber compositions show biological degradability. The mean fiber diameter is preferably 10 microns or less and is in particular between 2.5 and 5 microns.

According to a preferred embodiment the inventive glass-fiber composition contains 1 to 4 percent by weight titanium oxide.

According to another preferred embodiment the composition contains 1 to 4 percent by weight manganese oxide.

According to another preferred embodiment the composition contains 1 to 4 percent by weight zinc oxide.

According to another preferred embodiment the composition contains 0.5 to 5, in particular 0.5 to 3, percent by weight zirconium oxide.

According to another preferred embodiment the composition contains 0.5 to 4 percent by weight barium oxide.

In particular it is preferred to use mixtures of the oxides zirconium oxide, zinc oxide, titanium oxide, barium oxide and manganese oxide, in particular mixtures of two or three of these oxides.

Preferred embodiments are barium oxide in an amount of 1 to 4 percent by weight mixed with titanium oxide or zinc oxide.

In further preferred embodiments zinc oxide is mixed with titanium oxide and optionally additionally zirconium oxide, whereby the constituents may each be present in amounts of 1 to 3 percent by weight.

Further preferred embodiments are mixtures of zirconium oxide with zinc oxide, titanium oxide, barium oxide or manganese oxide, the constituents being present in amounts of 0.5 to 4 percent by weight, in particular 0.5 to 1.5 percent by weight.

With compositions containing zirconium oxide and/or barium oxide it is advantageous if the composition also contains 0.5 to 2 percent by weight fluorine and/or lithium oxide.

Aluminum oxide can be present in an amount of at least 0.1 percent by weight and in particular at least 0.5 percent by weight.

Phosphorus pentoxide increases biological degradability. The compositions preferably contain 0.1 to 2 percent by weight P_2O_5.

According to a further preferred embodiment the composition contains less than 2 percent by weight magnesium oxide.

The moisture-resistance of the inventive glass-fiber compositions was determined by a standard method known as

the DGG method. In the DGG method 10 g finely ground glass with a grain size between about 360 and 400 microns is held at the boiling point for five hours in 100 ml water. After quick cooling of the material the solution is filtered and a certain volume of the filtrate evaporated to dryness. The weight of the thus obtained dry material permits the amount of glass dissolved in the water to be calculated. The amount is stated in milligrams per gram of tested glass.

The biological degradability of the inventive glass compositions was tested by introducing 1 g of the glass powder, as described for the DGG method, into a physiological solution with the composition stated below and a pH value of 7.4:

$NaCl$	6.78
NH_4Cl	0.535
$NaHCO_3$	2.268
$NaH_2PO_4H_2O$	0.166
$(Na_3$ citrate$)$ $2H_2O$	0.059
Glycine	0.450
H_2SO_4	0.049
$CaCl_2$	0.022

Dynamic test conditions were selected as are described in Scholze and Conradt. The flow rate was 300 ml/day. The duration of the test was 14 days. The results are stated as percent of SiO_2 in the solution x 100 after 14 days.

The invention shall be described in more detail in the following with reference to examples.

Examples

Glass with the compositions stated in Tables I and II was melted.

All glass compositions could be processed satisfactorily by the centrifugal technique.

The second last line states the values determined by the DGG method. The last line states the values of biological degradability according to the method of determination described above.

Table I

Examples	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
SiO_2	54	53	53.5	54	53	54	53	53.5	53.5	53.5	55.5	52	53	52.5	54.7
Al_2O_3	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	1.9	1	0.5	0.5
CaO	8.5	8.5	8.5	8.5	8.5	8.5	8.5	8.5	8.5	8.5	8.5	8.0	8.5	8.5	8.5
MgO	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.6	3.5	3.5	3.5
Na_2O	17	17	17	17	17	17	17	17	17	17	15.8	14.5	17	17	14.0
K_2O	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.2	0.5	0.5	0.5	1.0
B_2O_3	13	13	13	13	13	13	13	12	12	12	12	14.5	13	12	12
TiO_2	2	2	2						2			1.0	2	2	1.0
MnO				2	2			2							
ZnO						2	2			1	1.5				
ZrO_2								2	2	2				2	
BaO											2	3.5			4.0
P_2O_5		1.0			1		1			1					
Fe_2O_3			0.3												
SrO_2															0.3
F													0.6	0.7	
Li_2O													0.4	0.3	
DGG	45	45	40	40	40	35	35	30	30	30	30	25	50	35	20
Biol. degradability	500	550	500	550	600	550	600	450	450	500	550	500	550	450	450

Table II

Examples	16	17	18	19
SiO_2	54	53.9	52.7	55.0
Al_2O_3	0.5	0.4	0.5	0.5
CaO	8.5	8.5	8.0	8.0
MgO	1.8	1.5	1.8	1.5
Na_2O	18.0	18.0	17.3	16.0
K_2O	0.7	0.7	0.7	0.5
B_2O_3	13.5	13.0	14.0	12.5
TiO_2	2.0		2.0	
MnO				
ZnO		3.0		
ZrO_2			2.0	2.0
BaO				3.0
P_2O_5				
Fe_2O_3				
SrO_2				
F				
Li_2O			0.4	0.4
Impurities	1.0	1.0	0.6	0.6

Claims

1. A glass-fiber composition that is biologically degradable, characterized by the following constituents in percent by weight:

SiO_2	50 to 60
Al_2O_3	less than 2
CaO + MgO	10 to 16
$Na_2O + K_2O$	14 to 19
B_2O_3	7 to 16
TiO_2	0 to 4
ZrO_2	0 to 5
ZnO	0 to 5
MnO	0 to 4
BaO	0 to 5
TiO_2, ZrO_2, ZnO, MnO, BaO	1 to 6
Fe_2O_3, SrO	0 to 2
F, Li_2O	0 to 2
P_2O_3	0 to 4.

2. The glass-fiber composition of claim 1, characterized in that the content of titanium dioxide is 1 to 4 percent by weight.

3. The glass-fiber composition of claim 1, characterized in that the content of manganese oxide is 1 to 4 percent by weight.

4. The glass-fiber composition of claim 1, characterized in that the content of zinc oxide is 1 to 4 percent by weight.

5. The glass-fiber composition of claim 1, characterized in that the content of zirconium oxide is 0.5 to 3 percent by weight.

6. The glass-fiber composition of claim 1, characterized in that the content of barium oxide is 0.5 to 4 percent by weight.

7. The glass-fiber composition of claim 1, characterized in that if the composition contains zirconium oxide and/or barium oxide it also contains 0.5 to 2 percent by weight fluorine and/or lithium oxide.

8. The glass-fiber composition of claim 1, characterized in that the composition contains barium oxide mixed with zirconium oxide, zinc oxide, titanium oxide and/or manganese oxide.

9. The glass-fiber composition of claim 1, characterized in that the composition contains zirconium oxide mixed with zinc oxide, titanium oxide, barium oxide and/or manganese oxide.

10. The glass-fiber composition of claim 1, characterized in that the composition contains less than 2 percent by weight magnesium oxide.

INTERNATIONAL SEARCH REPORT

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PCT/EP 95/01991

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C03C13/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C03C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	EP,A,0 588 251 (SCHULLER INTERNATIONAL, INC.) 23 March 1994 see Table 2, examples 5X and 6X see claims 1-3 ---	1,5,6, 8-10
A	EP,A,0 019 600 (OY PARTEK AB) 26 November 1980 see claim 1; example 3 ---	1,4,6-8, 10
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A	EP,A,0 412 878 (ISOVER SAINT-GOBAIN) 13 February 1991 see claims --- -/--	1

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GLASTECHNISCHE BERICHTE, vol. 64, no. 1, January 1991 FRANKFURT DE, pages 16-28, XP 000178832 R. M. POTTER ET AL. 'Glass Fiber Dissolution in a Physiological Saline Solution' see page 26 - page 27; table 2	1

INTERNATIONAL SEARCH REPORT

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